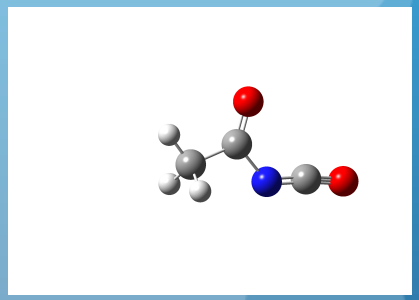
SUBMILLIMETER WAVE SPECTROSCOPY OF ACETYL ISOCYANATE : $CH_3C(O)NCO$



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Chemistry interest

- cis and trans isomerism:
  - most molecules with a conjugated double- bond structure seem to prefer the trans conformations (acrolein and derivatives of butadiene…).
  - Even the more analogous vinyl isocyanate prefer the trans configuration (C. Kirby, H.W. Kroto JMS. 70 (1978) 216.)
  - However, for vinyl azide it has been shown by relative intensity measurements of microwave spectra that the cis form is the more stable
  - the cis form is the more stable conformer in the gas, but the trans form is the stable form in the solid (K.A. Krutules, et al., J. Mol. Struct. 293 (1993) 23.)
- Isocyanate functional group (–NCO) is highly reactive and many chemicals containing isocyanate groups were used for the synthezises of polyurethanes.

Astrophysical interest

- Isocyanic acid, HNCO, was among the very early molecules to be detected in space.
  - In Sgr B2(OH) (L. E. Snyder and D. Buhl, ApJ, 177 (1972), 619 and D. Buhl et al. ApJ. 177, (1972), 625)
  - In TMC-1 (R. L. Brown, ApJ. 248, (1981), L119)
  - In three translucent clouds (CB 17 CB 24, and CB 228): (B. E. Turner, et al. ApJ. 518, 699–732 (1999)
- OCN^- is assumed to be in the grains (K. Demyk et al. A&A, 339 (1998), 553)
- CH_3COCH_3 is detected since 1987 Sgr B2 (F. Combes et al. A&A, 180, (1987), L13)

Astrophysical interest

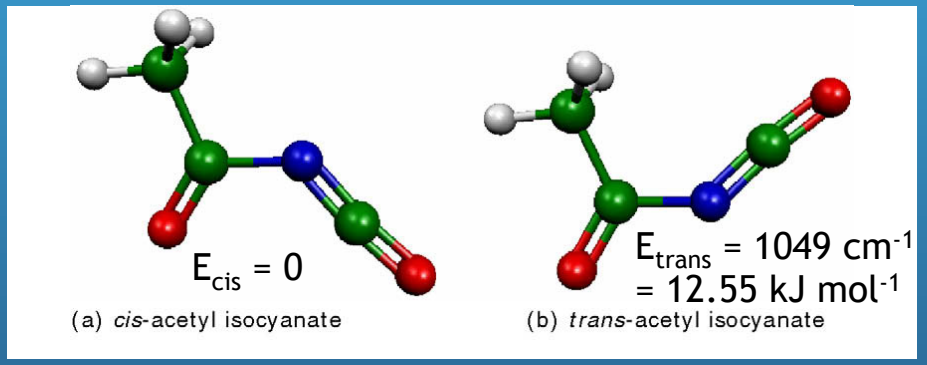
- Possible candidates for ISM detection: C_2H_3NO
  - CH_3NCO (V_3= 21 cm-1) (spectra up to 40 GHz: Koput et al, JMS, 1155, (1986), 131)
  - CH_3OCN (V_3=398 cm-1) (spectra up to 50 GHz: Skaizumi et al, J. Mol. Struct, 345, (1995), 189)
  - CH3CNO (symmetric top, spectra up to 230 GHz: Winnewisser et al. JMS, 91, (1982), 255)

  Not detected yet, but the most stable conformers are not studied in the millimeterwave domain: running projects in Valladolid (Alonso' s group)

- More complex: $C_3H_3NO_2$
  - CH_3CONCO (V_3=356 cm-1)
  - CH_3OCOCN (V_3=407 cm-1) (spectra up to 40 GHz: Durig et al, J. Chem. Phys., 96, (1992), 8062)

Previous studies

- MW spectra up to 40 GHz (B.M. Landsberg et al. J.C.S. Faraday, 76, 1208, 1980):
  - J_{max}=23 and $K_{a,max}$= 3
  - Dipole moment (Stark measurements): μ_a=0.954D μ_b=1.48D
  - 1st order internal rotation parameters determined
- MW spectra of $CD_3C(O)NCO$ and $^{13}CH_3C(O)NCO$ (Y. Uchida et al. J. Mol. Spectrosc. 256, 163, 2009)
  - Ab initio calculations
  - Molecular structure

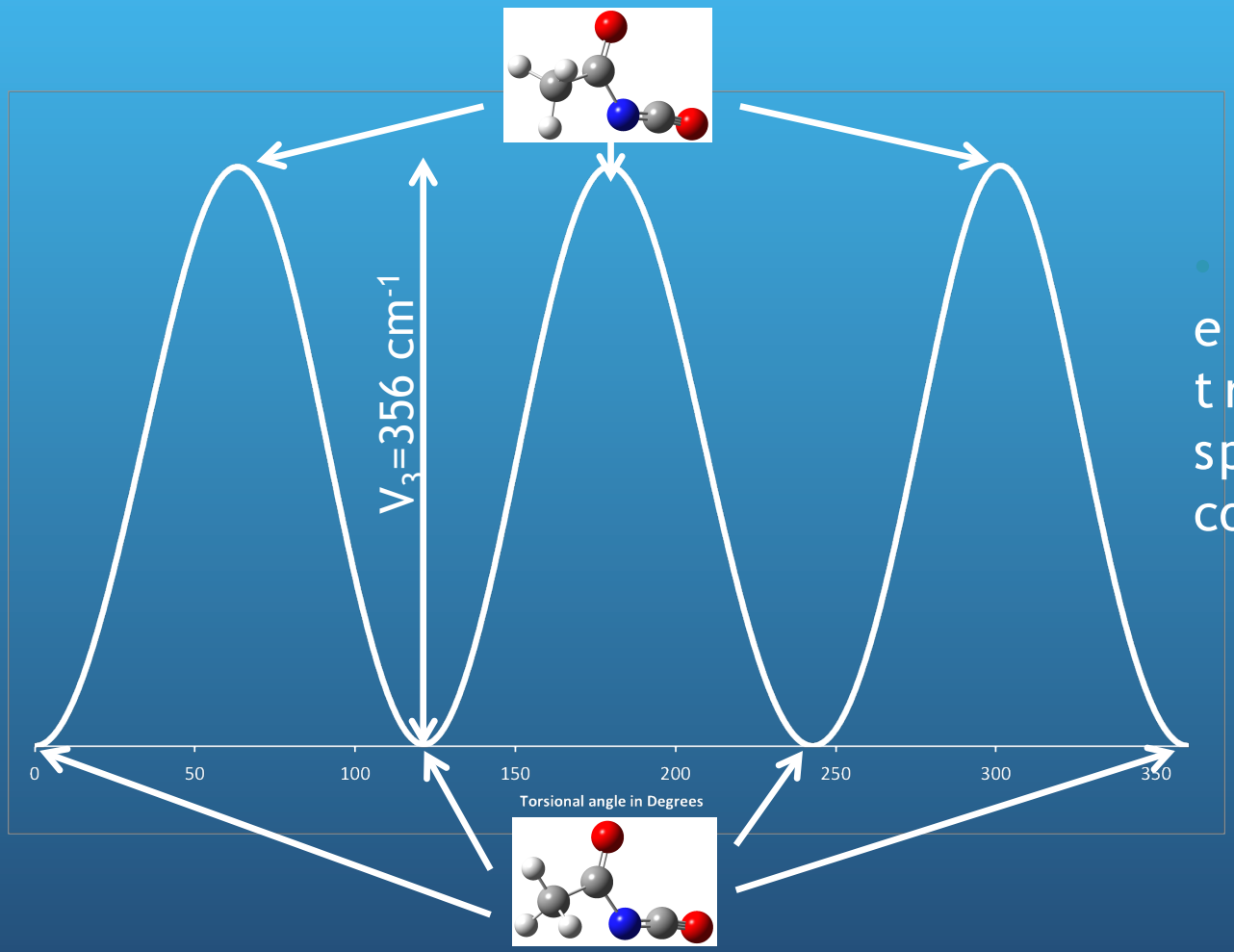


	V_3 in cm^{-1}	ρ
$HCOOCH_3$	373	0.08
CH3(ONCO	356	0.06

Similar case to methyl formate, should not be too difficult….

CH_3 internal Rotation

Methyl group is C_{3v} symmetry : $V(\alpha) = \frac{V_3}{2}(1 - \cos 3\alpha) + \frac{V_6}{2}(1 - \cos 6\alpha) + \ldots$



- Due to tunnel effect, the transitions are splitted into two components: A and E

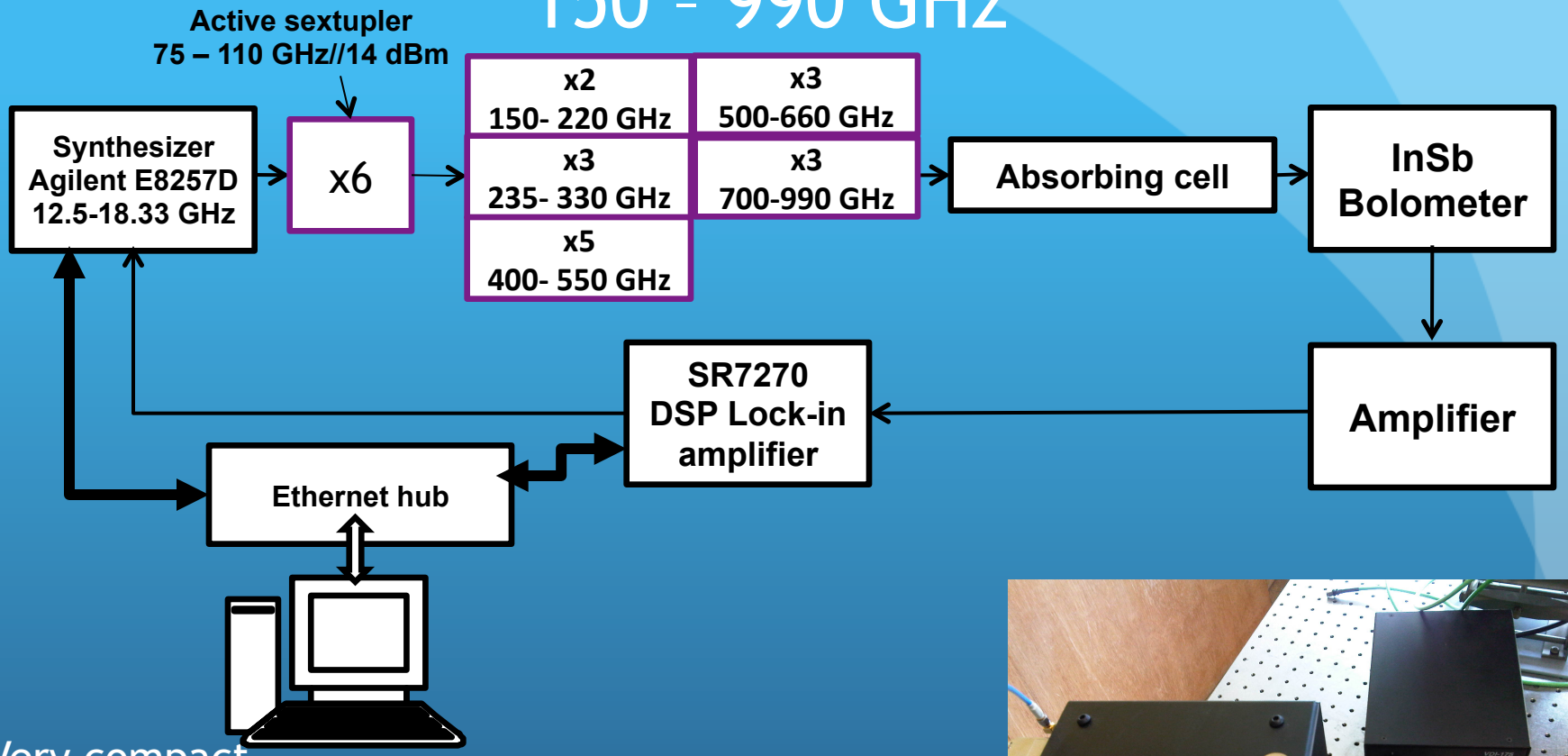
RAM method

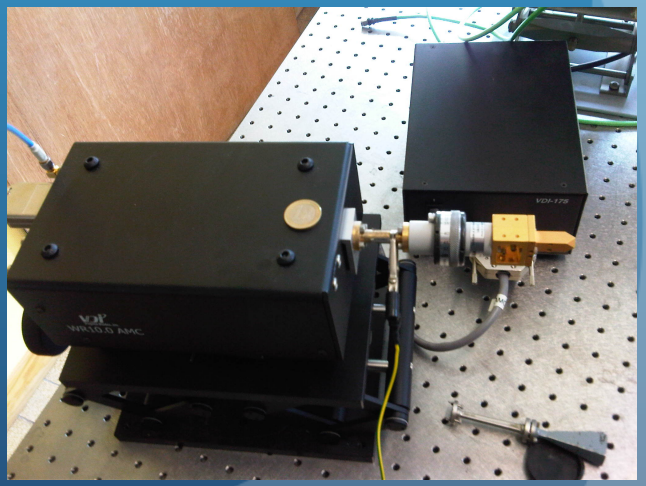
- The code used in these studies is « RAM36-code » (former V_6 code) from V. Ilyushin (Karkhov-Ukraine). The former name comes from the Toluene study (V. Ilyushin et al. J. Mol. Spectrosc 259, 26, 2010)
  - Include terms up to 12th order.

$$H = \frac{1}{2}\sum_{pqnkstl} B_{pqnkstl}[J^{2p}J_z^q J_x^n J_y^k p_\alpha^s \cos(3t\alpha)\sin(3l\alpha) + \sin(3l\alpha) \times \cos(3t\alpha)p_\alpha^s J_y^k J_x^n J_z^q J^{2p}]$$

- The code works also in V_3 mode:
  - 2-butynoic acid (V_3 = 1.009 cm^{-1}): V. Ilyushin et al. J. Mol. Spectrosc 267, 186, 2011
  - Acetaldehyde (V_3 = 407.6 cm^{-1}): I.A. Smirnov, J. Mol. Spectrosc 295, 44, 2014

Solid state sources spectrometer: 150 – 990 GHz



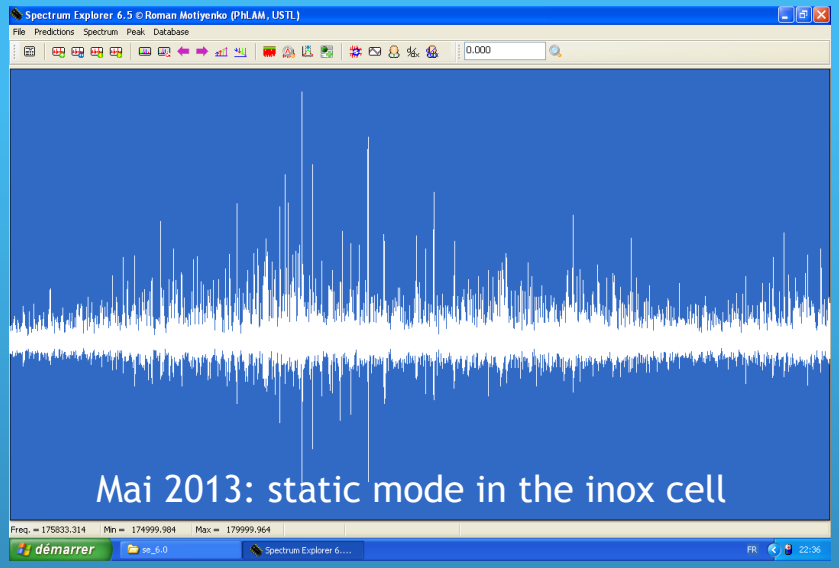


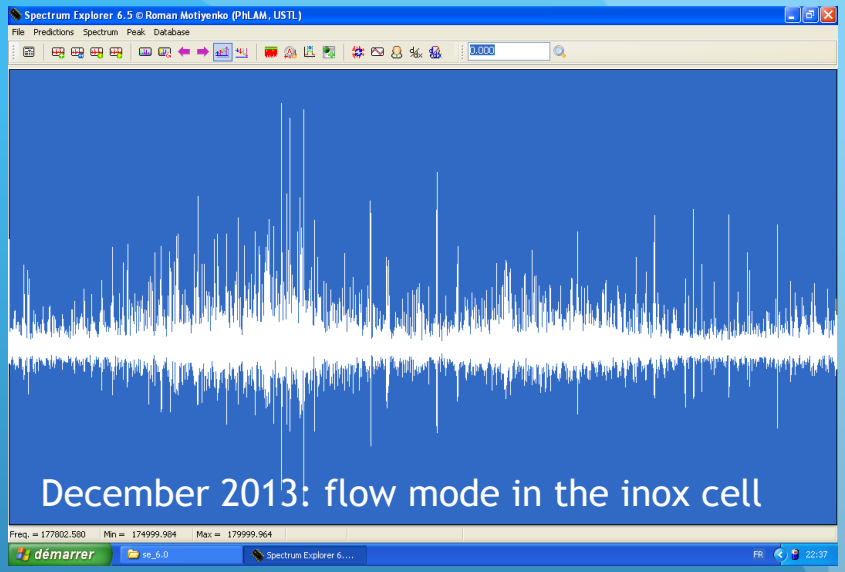
- Very compact
- power : 50 mw – 5mW)
- Broad band : Assigment easier with series, like in I. R.
- Full coverage with high resolution in 5 days

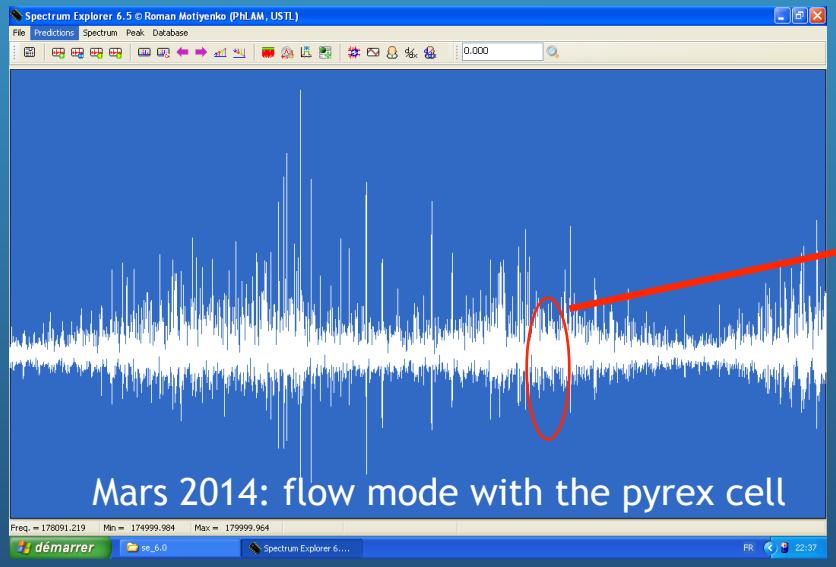
Experimental details

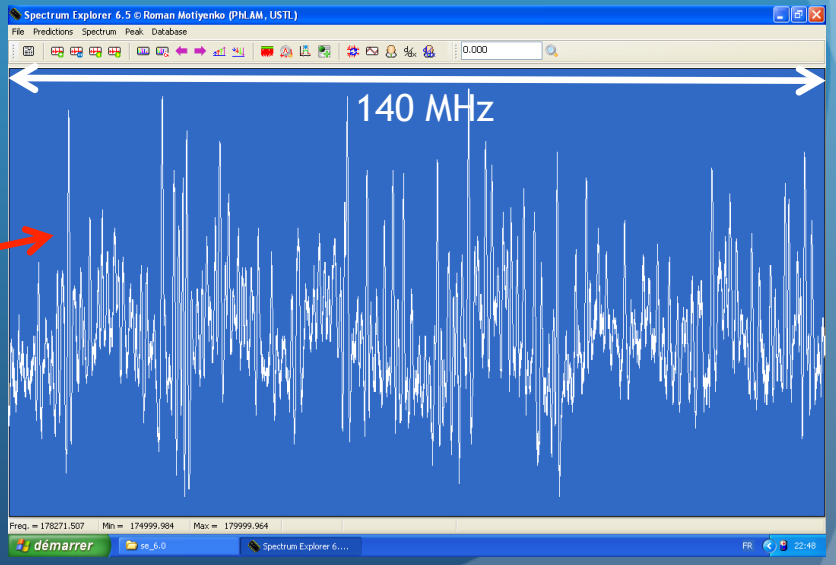
- The synthesis is well known: Acetyl isocyanate was prepared by the reaction of acetyl chloride with silver cyanate (***Rodd's Chemistry of Carbon Compounds*** (Elsevier, **Amsterdam, 2nd edn, 1965), vol. I, part C, p. 360**)
- The compound is relatively stable, could be stored in the fridge (-20°C) for months, but the spectra obtained have poor signal to noise ratio. We thought it was reactive with metal, it was recorded 3 times
  - Mai 2013: static mode in the inox cell
  - December 2013: flow mode in the inox cell
  - Mars 2014: flow mode with the pyrex cell

175-180 GHz spectra





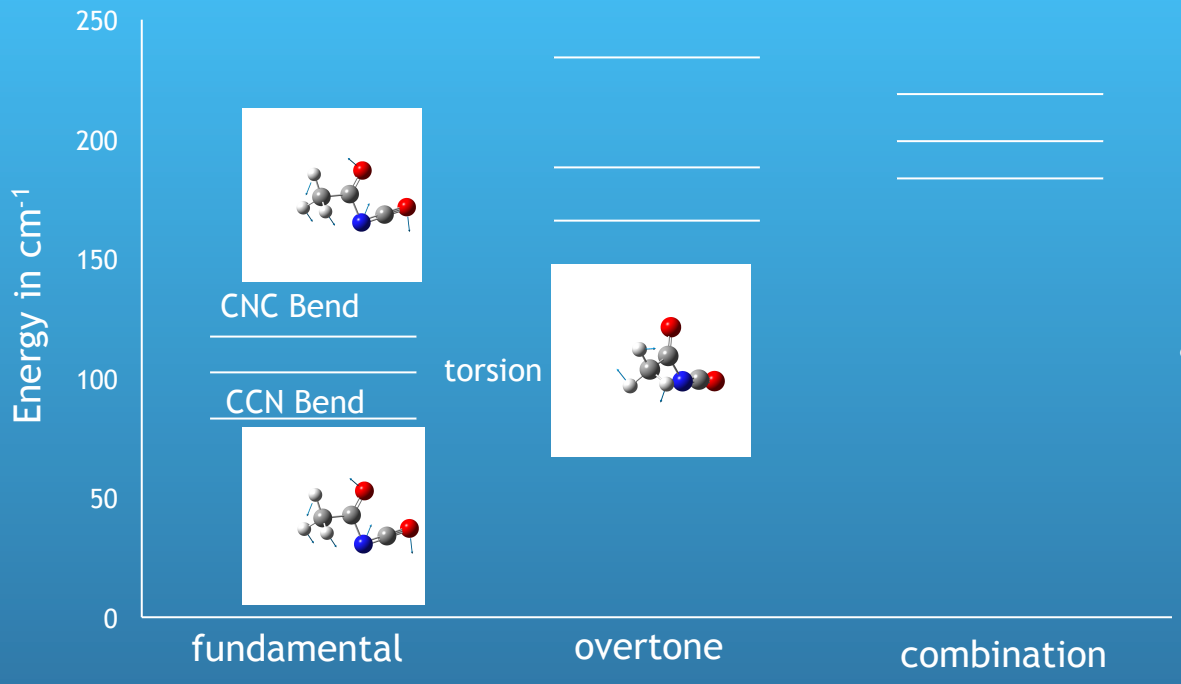




Not noise but huge number of lines!

Vibrational energy levels up to 250 cm^{-1}

(from B3LYP/6-311G++(3df,2pd) anharm force field)

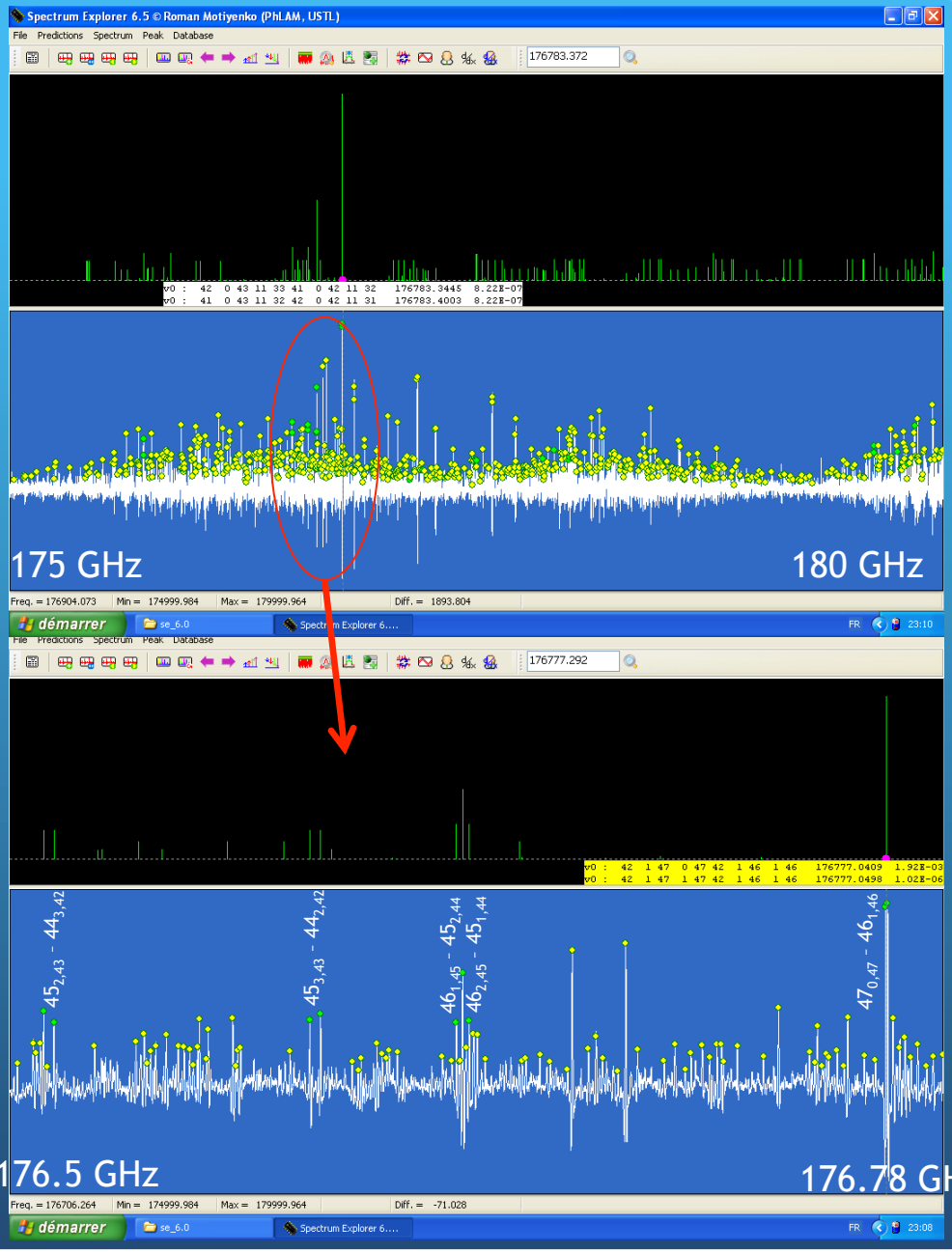


- 9 energy levels below 250 cm^{-1}: floppy!

- In particular 3 levels at 83, 102 and 117 cm^{-1}, spectra difficult to assign: Levels are interacting together and certianly with g.s.
- In fact: not so big surprise considering the « extremely floppy » HNCO

Spectra

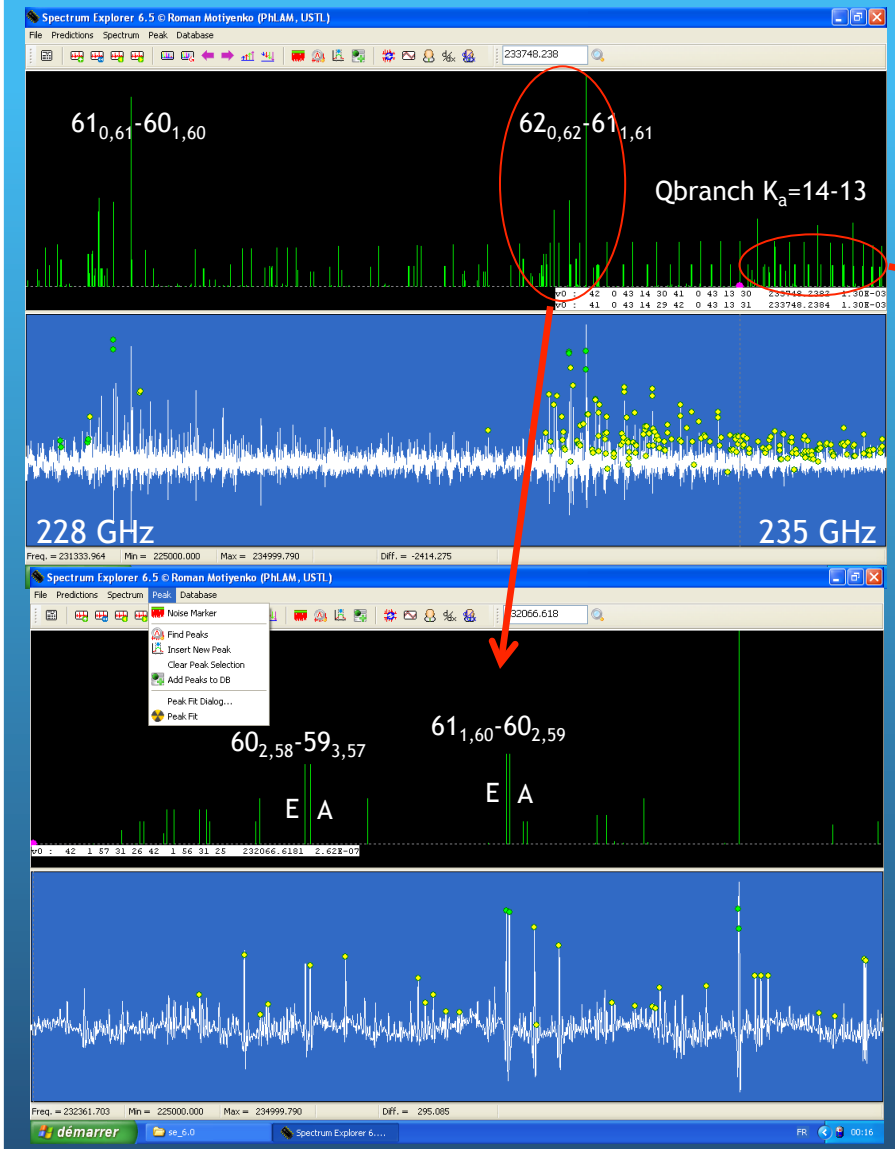
- Spectra wil be very dense, considering Boltzman distribution: at 300 K the relative intensity of the 3 excited states (83, 102 and 117 cm^{-1}) are respectively: 67%, 61% and 59%. At 234cm-1 ($2\nu_{CNCbend}$), still 32%
- The vibrational contribution to the partition function will be relatively important: spectra of the ground state will not be very intense



Assignment

- The most intense lines don't have great signal to noise ratio
- Intensity decrease fastly with K_a, close to prolate limit case

Assignment


Spectrum Explorer 6.5 © Roman Motiyenko (PhLAM, USTL)
File Predictions Spectrum Peak Database
$61_{0,61}$-$60_{1,60}$
$62_{0,62}$-$61_{1,61}$
Qbranch K_a=14-13
228 GHz
235 GHz
Noise Marker
Find Peaks
Insert New Peak
Clear Peak Selection
Add Peaks to DB
Peak Fit Dialog...
Peak Fit
$60_{2,58}$-$59_{3,57}$
$61_{1,60}$-$60_{2,59}$
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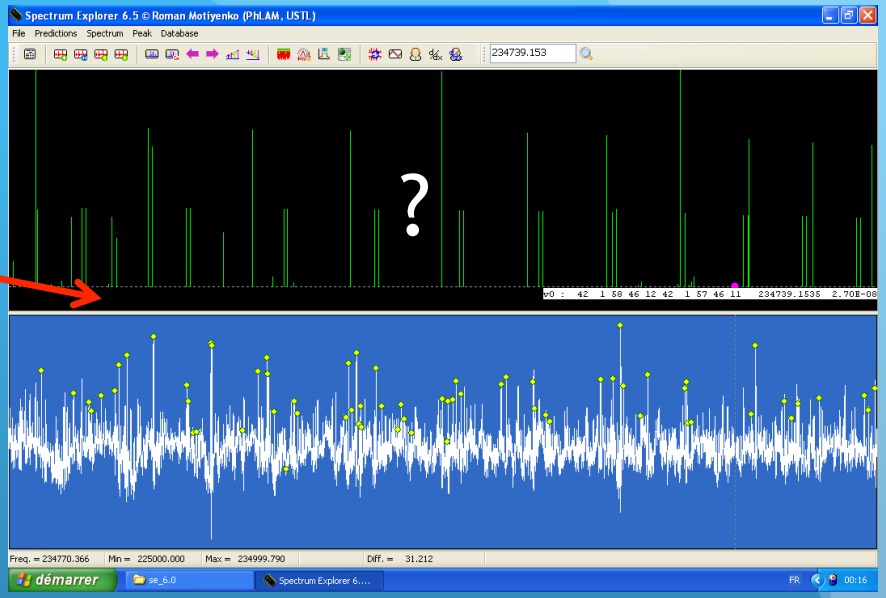
Spectrum Explorer 6.5 © Roman Motiyenko (PhLAM, USTL)
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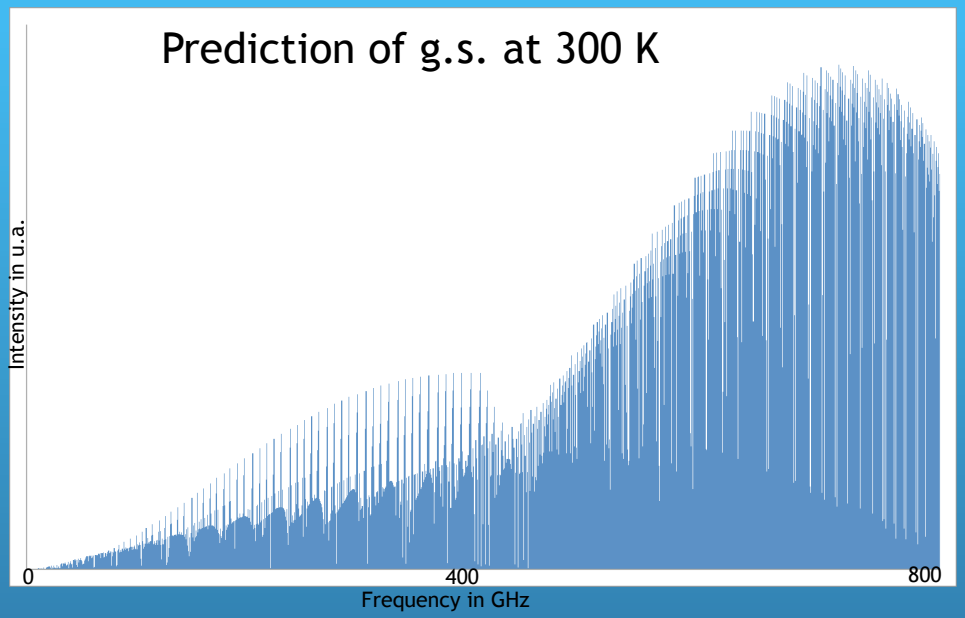
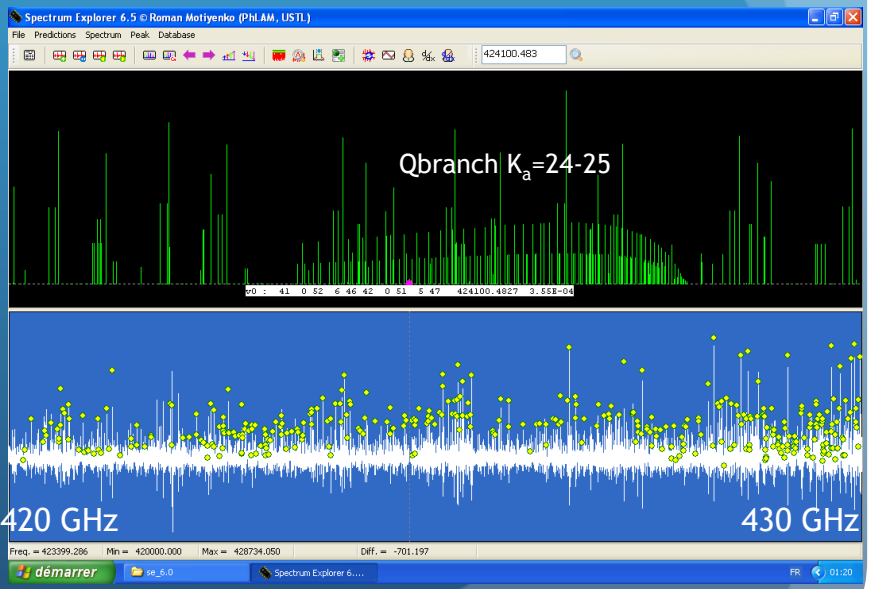
Submillimeterwave spectra



- Even if the molecule is heavy (85g.mol-1), spectra is intense in the submillimeterwave region
- Intensity of μ_B lines increase with Freq.

- Spectra measured up to 480 Ghz, if assignment is positive, we will increase the range



Results

	This work	Landsberg et al.
A (GHz)	10.62204(27)	10.6234(13)
B (GHz)	2.37146(29)	2.3690(13)
C (GHz)	1.863406(26)	1.8628616(37)
F (GHz)	168.783 (fixed)	168.783 (fixed)
ρ	0.05880(13)	0.05871(17)
V_3 (cm-1)	356.48(26)	356.26(42)
$2D_{ab}$	-2231.5(21)	-2217.3(96)
D_J (kHz)	0.32552(32)	0.380(32)
D_{JK} (kHz)	8.803(18)	9.270(68)
D_K (kHz)	6.40(21)	
d_j (kHz)	0.01035(16)	0.0106(19)
d_k (kHz)	2.825(6)	2.89(7)
Number of parameters	13	
N_{lines}; J_{max}; $K_{a,max}$	203 - 70 - 6	106 - 23 - 3
Wrms/rms rms (Landsberg et al.) rms (Lille)	0.71/73kHz 116 kHz 34 kHz	0.71/107 kHz

- Rotational dependance of V_3 and one sextic cent. dist also fitted:15 lines/param
- 1st torsionnal state analysis is necessary to fit F

Conclusion - Perpectives

- Assignment is still in progress for higher K_a values and up to 480 GHz
- Treatment of the bending and torsional modes could be possible in the near future: V.V. Illyushin, I. Kleiner and J. Hougen are coding the interactions…

Conclusion- Perspectives

- The prediction for the lines which could permit its ISM detection is accurate anough: its search in in progress in ORION with J. cernicharo survey or later with ALMA…

Aknowledgements

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And many thanks for your attention